

COAL: CROSS-LINKED NETWORKS OR ASSOCIATED STRUCTURES?

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Introduction

For many years the "standard model" for coal structure has essentially considered most coals to consist of covalently cross-linked networks with a cross-link density and "sol" fraction that varies systematically with rank (this model excludes anthracites and high rank coals that are more graphitic in their structure). Recently, this view has been challenged on a number of grounds. One view, based on some seminal and very important experiments on the mechanical response of swollen coal particles, is that coal is indeed a macromolecule but the network essentially consists of entangled rather than covalently linked chains (1). We have remained somewhat skeptical of this model because it would suggest that there should be a solvent that could completely dissolve coal. More on this later. Another fairly recently proposed model considers coal to be an associated structure, held together by secondary forces acting in some undefined cooperative manner (2-6). Although space in this preprint does not allow us to fully review the evidence for this view, it is largely based on three lines of evidence

1) There is a solvent induced association that occurs upon soaking in organic solvents 2) There is an increase in extraction yields using certain mixed solvents 3) Experiments involving the swelling of extracts compared to the swelling of residues

The latter experiments have been largely interpreted in terms of secondary forces such as hydrogen bonds acting as cross-links, thus by extension indicating that the parent coal itself may be held together by such forces.

We have addressed this latter point in a note (7). If, for example, one were to take a pyridine soluble extract and then try to swell it in pyridine, one would not get any useful result, because the extract would simply redissolve. In this type of work the extracts are placed in contact with a *poor solvent*, like benzene or methanol. The phase behavior of such mixtures is such that there will be a solvent rich phase (e.g., benzene with some dissolved extract) and a solvent poor phase (a "swollen" extract rich phase). It is not our intention in this paper to rehash this issue but to consider some of the other evidence that has been cited as favoring an associated structure. Some recent work in the polymer literature will also be discussed because of the light it throws on what role secondary interactions can play in terms of forming crosslinks.

Solvent Soaking and Extraction of Coal

Nishioka (2-5) has argued that the evidence for associative equilibria in coal has not been fully recognized. The basis for this view is the change in extraction yields upon pre-soaking in pyridine (or other solvents) and the enhanced yields obtained in multi-step extraction. These experiments, however, are seriously flawed. Take, as an example, the soaking experiments. A coal is soaked in pyridine for various periods of time. The pyridine is evaporated and the treated coal is washed with methanol. This coal is then Soxhlet extracted with pyridine. The yield of soluble material obtained in this latter step is found to be less than the yield obtained by Soxhlet extraction of the original untreated coal. It is then argued that there is some solvent induced conformational change that results in the coal being more "associated" than the original structure.

We have repeated these experiments with an Illinois #6 coal and obtained very similar results. We found 20.1% of the weight of the original coal could be extracted with pyridine (the residue accounted for 80.7 wt%, giving a total of 100.8% because of tightly bound residual pyridine). The pyridine soaked coal only gave an extraction yield of 16.9%, however, an apparently significant reduction. The problem is that Nishioka ignored the material that dissolves in the methanol washing step, which accounts for 2.8% of the original coal, giving a total extraction yield of 19.7%, within error of the extraction yield of the original coal. Of course methanol by itself does not extract appreciable amounts of soluble material from the original coal, but this is because it does not swell the coal to any detectable amount, so that low molecular weight material that may be soluble remains trapped in the network. Upon treating with pyridine, soluble material is extracted from the coal particles into the solvent phase and upon evaporation of solvent this material remains sitting on the surface of the coal particles. A portion of this, probably the low molecular weight end, can then be dissolved in the methanol wash step. In other words, the arguments concerning the effect of soaking immediately collapse once a complete mass-balance is performed.

The evidence concerning multi-step extraction is similarly flawed. For example, Nishioka asserts, with no evidence, that covalent bonds are not broken in these experiments. However, reactive solvents, such as phenol at 180°C, are used! At these temperatures phenol can break ether linkages.

Experiments involving mixed solvents, particularly the CS₂/NMP mixture used by Iino and co-workers (8), provide far more compelling evidence that many coals have a much larger soluble fraction than originally suspected. This does not mean that they are associated structures simply held together by secondary forces, however. Figure 1 shows the extraction yields obtained from just U.S. Eastern and Interior coals (we have found in previous work that comparing coals from similar sources gives superior correlations). In this figure the yields obtained using a CS₂/NMP mixture are compared to pyridine extraction yields as a function of coal rank. The first thing to note is that many samples of equivalent rank give comparable yields. However, a large proportion gave significantly high yields, the largest being an Upper Freeport Coal giving a 54% extraction yield in CS₂/NMP. (Iino et al (8) also reported a Zao Zhuang coal that gave a 65% extraction yield). As we mentioned above, this does not mean that these coals are purely associated structures. At the gel point in the formation of polymer networks only about 16% of the material (by volume) needs to be in the "gel" or network phase to give a continuous structure, the rest can be the "sol" or soluble phase (9,10). Furthermore, it would not be surprising, giving the heterogeneous character of coal, that a few coals are indeed significantly different in their structure to most of their counterparts, being largely soluble in the appropriate solvents. Finally, there are other compelling reasons to believe that coal is not a collection of relatively small molecules held together by secondary forces such as hydrogen bonds and these relate to the nature and character of these interactions.

The nature of cross-linking and cooperative processes in physical gels

There are various types of cross-links that can exist in networks. It is useful to subdivide these into two categories, "point" cross-links and junction zones. In the first category are covalent cross-links, entanglements and specific interactions such as hydrogen bonds. The first of these, covalent linkages, can be considered "permanent", in the sense that if we confine our experiments to conditions of temperature, stress, etc., where bond rupture does not occur, then they confer certain elastic properties on the network (e.g., reversible deformation). Entanglements and non-covalent linkages are dynamic, so that in the "melt" or liquid state (i.e., above the T_g of the system), they have a "lifetime" or, more precisely, there is a relaxation time associated with their behavior. Thus under fast loads a non-covalently cross-linked polymer like "silly putty" behaves elastically, because the rate of loading is much faster than the "disentanglement" time. Under slowly applied loads the material deforms permanently, because the chains have time to disentangle.

This brings us to secondary interactions such as hydrogen bonds; can they act as crosslinks? We have to be careful about semantics here. Of course, there is a "network" of hydrogen bonds in materials such as coal, but in order for them to act as cross-links they must maintain their integrity during the course of a deformation experiment (e.g., swelling), thus causing the interlinked segments to be displaced in such a way as to maintain a certain spatial relationship with respect to one another (i.e., there are configurational constraints relative to a non cross-linked system). As with entanglements, this comes down to the dynamic properties of the cross-link relative to the time frame of the mechanical experiment. For small molecules in the liquid state the lifetime of hydrogen bonds appears to be in the range 10⁻⁵ to 10⁻¹¹ secs, much too short to act as a cross-link. In macromolecular systems the dynamics of the hydrogen bond can be coupled to those of the chain, so that the situation may be very different. The work of Stadler and co-workers (11-13), however, demonstrates unequivocally that at temperatures well above the T_g the lifetimes are still very short (~ 10⁻³ to 10⁻⁶ secs, depending on the experiment).

Stadler and his group have published an extensive body of work concerning the effect of hydrogen bonds on mechanical and rheological properties. They introduced urazole groups, which form hydrogen bonded pairs with an enthalpy of about -7 kcal/mole (i.e., somewhat stronger than most of the hydrogen bonds found in coal), into various elastomers and compared properties to those of the unmodified rubbers. The transient network formed by the hydrogen bonds was found to affect viscoelastic properties through an apparent increase in the viscoelastic effective molecular weight, but the equilibrium network modulus remained unaffected (i.e., the hydrogen bonds were not behaving like covalent cross-links). In a theoretical analysis Leibler et al. (14) demonstrated how the properties of these transient networks depend upon the dynamics of the hydrogen bonded complex. At frequencies that are higher than the characteristic frequency of the complex, the hydrogen bond acts like a covalent cross-link, but at lower frequencies they hydrogen bonds simply retard the terminal relaxation. However, as a system is cooled through the T_g there is a point where the dynamics are such that a hydrogen bond could act as a cross-link (11-13).

Now we must consider the implications of this work for coal extraction and swelling. The quantity we work with is the change in free energy of the swollen coal/solvent gel relative to that of the initial pure coal and pure solvent. The initial coal is a glassy solid. Are the hydrogen bonds and perhaps other interactions acting as cross-links in this state? If we neglect various relaxation processes we can argue that all contacts are essentially frozen in place, so they are all cross-links! What is important is this; we must consider the change in free energy on going to the swollen state. Larsen and co-workers (15,16) have demonstrated that swollen in a good solvent a coal such as Illinois #6 has a T_g of about 210°K, well below room temperature (naturally, we are only discussing coals that are capable of appreciably swelling in a good solvent). In this state point interactions such as hydrogen bonds (and anything weaker such as π - π^* interactions) cannot act

as cross-links in the time-frame of a swelling measurement. Covalent cross-links, however, contribute to the free energy through terms that account for the distribution of chain configurations between cross-link points and the distribution of cross-link junctions over the volume of the swollen gel relative to volume of the initial coal (at least in the Flory model). In other words, it is only those contacts that are crosslink points or junctions in both the original pure coal and the swollen coal gel that determine the free energy change. Other types of contacts contribute to the free energy through mixing terms, where a proportion of coal/coal contacts are replaced by coal/solvent contacts to an extent that depends upon composition. We have made this point before, although not in this way, and demonstrated how coal will not swell in a non-hydrogen bonded solvent because the mixing part of the free energy changes are unfavorable, not because the hydrogen bonds act as cross-links (i.e., if the coal and solvent don't mix, the hydrogen bonds don't break!)

This finally brings us to the question of whether secondary forces can act in a cooperative manner to give so-called "junction zones". In various coal papers such cooperative processes are often invoked, but never specified. This should be against the law, because the types of cooperative processes that occur in physical gels are well-known and occur through specific identifiable mechanisms, such as the formation of triple helical regions, as in gelatin; microcrystalline regions, as in poly(vinyl chloride) gels; or by the intersection of a liquid-liquid phase separation and a glass transition, as in polystyrene gels formed upon cooling certain solutions (see reference 17). These processes are all subject to physical characterization and detection. If cooperative processes are to be invoked in coal, their nature must be specified, together with the evidence leading to this conclusion, otherwise we are left with the "standard model"; coal is a covalently cross-linked network.

Acknowledgments

The authors gratefully acknowledge the support of the Office of Chemical Sciences, U. S. Department of Energy, under grant No. DE-FG02-86ER13537.

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Plot of the extraction yield versus carbon content of coals

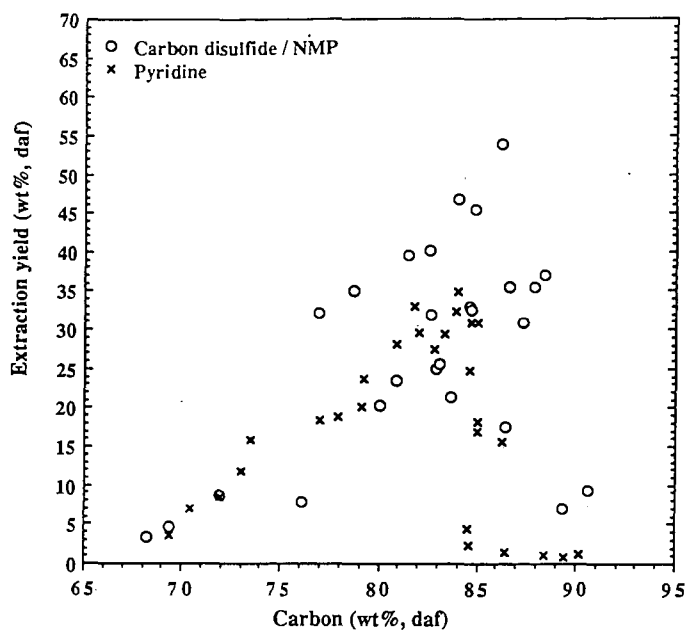


Figure 1.